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Alternating Copolymerization of Butadiene-1,3 with Acrylonitrile

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This review deals with the alternating copolymerization of several kinds of binary monomers such as olefins, conjugated dienes and polar vinyl monomers using Lewis acid type catalyst. Mainly, alternating copolymerization of butadiene with acrylonitrile using the binary catalyst of organoaluminum compound and transition metal compound, and the feature of the physical properties of the copolymer will be described. We succeeded to prepare the new alternating copolymer of butadiene with acrylonitrile, which is superior in toughness, elasticity and oil resistance to conventional nitrile rubber.

I. INTRODUCTION

It is only within the last few years that several publications of alternating copolymerization have been so many. The advances in the understanding of the mechanism have been so rapid that it is worth reviewing again at this time. This review deals with the new research field and attempts to point out some areas where new investigations on the alternating copolymerization of butadiene—acrylonitrile mainly carried out in our laboratory would be helpful.

II. GENERAL SURVEY

1. Alternating Copolymerization of Olefins

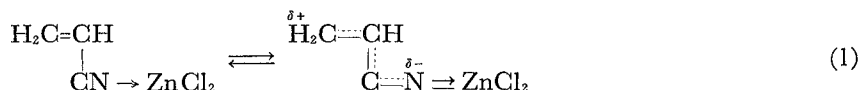
Already, G. Natta *et al.* succeeded in preparing copolymers of olefins containing an internal double bond or of cyclic olefins with ethylene.¹⁻³⁾ The copolymer having a high content of butene-2 unit was obtained by VCl_4 -Al(hexyl)₃ catalyst under the polymerization conditions with high concentration of butene-2 and with very low ethylene concentration. The infrared absorption spectrum at $13.2\ \mu$ of the copolymer containing about 50 mole % of butene-2 suggests that the copolymer is the alternating one. The ethylene—cis-butene-2 alternating copolymer was crystalline. However, the ethylene—trans-butene-2 alternating one was not crystalline. In the case of cyclopentene, under low partial pressure of ethylene, copolymer of nearly 1:1 composition was obtained. The copolymer showed a high crystallinity and the characteristic absorption band at $13.2\ \mu$ due to $(-CH_2-CH_2-)$ unit. These suggest that the copolymer has a regularly alternating structure of ethylene and cyclopentene monomeric unit. The alternating copolymerization may be mainly controlled by the steric effect between the growing chain end and the attacking monomer.

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Recently, binary copolymerizations of ethylene, propylene and butene-1 were studied by Italian group.⁴⁾ The copolymer prepared by syndiotactic catalyst such as $\text{VCl}_4\text{—AlEt}_2\text{Cl}$ or $\text{VCl}_4\text{—AlEt}_2\text{Cl}$ -anisole was 1:1 copolymer and was nearly alternating one. On the other hand, the copolymer prepared in the presence of the non-stereospecific or isotactic catalyst was closed to random. From these results, it was estimated that the syndiotacticity is due to the steric interaction between entering monomer and the last unit of the growing chain end and that the isotacticity is due to the steric interaction between monomer and the counter-ion. This is very interesting information compatible with our concept in the stereospecific polymerization⁵⁾ and may be valid for the alternating copolymerization mechanisms.

2. Alternating Copolymerization of Olefin with Polar Vinyl Monomer

The free radical polymerization of polar monomers such as acrylonitrile, methyl methacrylate, methyl acrylate and vinyl acetate *etc.* in the presence of metal halides has been extensively investigated.⁶⁻⁹⁾ The formation of complex between the polar group and the metal halide enhanced the reactivity of the monomer. The complex formation seems to cause the delocalization of the electron in the double bond of the complexed monomer as shown in equation (1).



This mechanism was proposed by the results of Imoto *et al.*⁶⁾ and was discussed in terms of the molecular orbital calculation by Tazuke *et al.*^{10,11)}

The effect of ZnCl_2 on the radical copolymerization of methyl methacrylate with butene isomers and of acrylonitrile with allylic compounds was dealt with by Imoto *et al.*¹²⁾ The results are characterized by the incorporation of large amounts of the butene isomers or the allylic compounds in the presence of ZnCl_2 . The polymer compositions, however, varied depending upon the monomer compositions. On the other hand, Hirooka *et al.*¹³⁾ found that an α -olefin and acrylonitrile complexed with organo-aluminum halide copolymerizes spontaneously at low temperature to give a 1:1 copolymer as shown in Table 1.

Similarly, several kinds of the alternating copolymer have been prepared in the presence of a halogeno-organometallic compounds or a metal halide; α -olefin or styrene with methyl acrylate or methyl methacrylate by an organo-aluminum halide,¹⁴⁾ styrene or α -methyl styrene with acrylonitrile or methyl methacrylate by ZnCl_2 -radical initiator system,¹⁵⁾ styrene with methyl methacrylate by ZnCl_2 -2-methyl pentanoyl peroxide,¹⁶⁾ styrene with acrylonitrile, methacrylonitrile or methyl methacrylate by ZnCl_2 or by SnCl_4 , AlCl_3 or BF_3 with UV irradiation,¹⁷⁾ ethylene with vinyl acetate by $\text{ZnCl}_2\text{—AlEt}_3\text{—CCl}_4$ system.¹⁸⁾

Already, the formation of molecular complex between the electron donating monomer and the electron accepting monomer is under consideration as the determining factor in the conventional radical alternating copolymerization of styrene with maleic anhydride¹⁹⁾ or sulfur dioxide²⁰⁻²⁴⁾ with olefins and dienes. On the other hand, Walling *et al.*^{25,26)} pointed out a relationship between molecular complexes formation and the alternating tendency and assumed the alternation involving an intermole-

Table 1. Copolymerization of Acrylonitrile with Olefins¹³

Olefin (g)	AN (g)	Organoaluminum halide (mmole)	Solvent (n-heptane) (ml)	Temp. (°C)	Polymer				
					Yield (g)	[η] (dl/g)	Elementary analysis* (%)		
							N	Composition of polymer	
Ethylene (300)	6	AlEt _{1.5} Cl _{1.5}	150	20	-78	1.46	—	17.80 (17.27)	1 : 1
Propylene (1500)	30	AlEtCl ₂	575	100	-78	20.1	3.00	14.41 (14.72)	1 : 1
Hexene-1 (10)	2	AlEt _{1.5} Cl _{1.5}	50	20	0	0.67	0.15	10.64 (10.21)	1 : 1
Octa- decene-1 (15)	2	AlEt _{1.5} Cl _{1.5}	50	—	25	0.15	0.08	4.55 (4.58)	1 : 1
Iso- butylene (15)	1.5	AlEt ₂ Cl	25	20	-78	0.81	2.08	12.26 (12.83)	1 : 1
Styrene (10)	2	AlEt _{1.5} Cl _{1.5}	25	20	-10	2.93	1.88	9.02 (8.91)	1 : 1

* Figures in parentheses indicate the value calculated for 1:1 copolymer.

cular semipolar bond stabilized by a resonance energy. Now, we are reexamining²⁷⁾ the possibility noted by Walling. The participation of Diels-Alder type intermediates in the emulsion polymerization of butadiene with methyl methacrylate was considered by Hill *et al.*²⁸⁾

As mentioned above, the alternating copolymerization of the olefinic compound with the polar vinyl monomer was succeeded in the presence of Lewis acid or Friedel-Crafts type metal halide. The Lewis acid and metal halide may enhance the electron accepting power of the complexed polar vinyl monomer and consequently the electron transfer from the former monomer to the latter one may occur more readily. As a result, there might be an increased tendency for the alternation in the copolymerization. This may be one of the possible explanations, and will be discussed in detail elsewhere.²⁹⁾

3. Alternating Copolymerization of Dienes

The first basic approach to the alternating copolymerization of butadiene with ethylene was reported by G. Natta *et al.*³⁰⁾ However, the molecular weight of the alternating copolymer of butadiene-ethylene prepared by VCl₄-Al(iso-Bu)₃-Al(iso-Bu)₂Cl-anisole catalyst was rather low. The copolymer yield based on the catalyst used was also very poor. A few years after that the research group of Nihon Oil Co. succeeded to prepare the alternating copolymer of butadiene-ethylene by TiCl₄-AlEt₃-AlEt₂Cl catalyst by adopting the condition with the slow feed of ethylene.³¹⁾

On the other hand, copolymerization of butadiene with propylene in place of ethylene was tried by AlEt₃-TiCl₄ catalyst,³²⁾ but the copolymer obtained seems to be a block one. Recently, Tsuruta and Ishizuka copolymerized butadiene and propylene using AlEt₃-TiCl₄ together with polypropylene oxide,³³⁾ the latter of which may act as a randomizer and yields a more random copolymer than the

copolymer prepared in the absence of it. Furukawa *et al.*³⁴⁾ found that in the presence of $\text{VOCl}_3\text{-AlEt}_3\text{-AlEt}_2\text{Cl}$ system butadiene and propylene copolymerize to an 1:1 copolymer, yielding the low molecular weight polymer, and the catalytic activity was rather low.

Recently, it is reported that acrylonitrile-isoprene copolymer could be prepared by azobis-isobutyronitrile as free radical initiator when ZnCl_2 is used as complexing agent.³⁵⁾ The acrylonitrile was utilized in considerable excess to dissolve the acrylonitrile- ZnCl_2 complex. The copolymer composition was nearly 1:1. It is seemingly alternating one, but the polymer is almost insoluble.

As a special example of alternating copolymerization, so-called equibinary copolymerization of isoprene by Co salts-Grignard reagent-alcohol system and of butadiene by $\text{Ni}(0)$ complex- CF_3COOH system were reported.³⁶⁾ These copolymers contained nearly equimolar amounts of cis-1,4/3,4 isomeric units and cis-1,4/trans-1,4 isomeric units, respectively.

Few years earlier than this, Furukawa *et al.* found³⁷⁾ that the polymerization of butadiene with $\text{Co}(\text{acac})_3\text{-AlEt}_3\text{-H}_2\text{O}$ system yields similar cis-1,4/1,2 equibinary copolymer. Finally, the author will note that Furukawa *et al.*^{38,39)} and Gaylord *et al.*⁴⁰⁾ succeeded independently in finding the preparative method of the alternating copolymer of butadiene with acrylonitrile, although the former was rubbery soluble polymer whereas the latter powdery insoluble one. There will be a detailed mention of it in following section.

III. ALTERNATING COPOLYMERIZATION OF BUTADIENE WITH ACRYLONITRILE

1. Alternating Copolymerization of Diene with Polar Vinyl Monomer

In some the early work, it was suggested that the donor monomer—acceptor monomer interaction was recognized as playing an important role in a conventional radical copolymerization.¹⁹⁾ The authors found that the alternating copolymerization of butadiene with acrylonitrile was succeeded in the presence of the alkylaluminum

Table II. Copolymerization of Diene with Acrylonitrile or with Methyl Methacrylate by $\text{AlEtCl}_2\text{-VOCl}_3$

Monomer $M_1\text{-}M_2$	M_1 (mole-%) in feed	Solvent	Polymn. temp. (°C)	Yield (%)	Polymer	
					M_1 (mol-%) Obs	Calc.*
IP-AN	25.0	—	0	16.3	51.5	51.2
IP-AN	66.7	tetrachloro- ethylene	0	24.0	52.1	60.6
PD-AN	25.0	—	0	4.1	53.8	—
BD-MMA	66.7	—	25	19.3	50.5	66.7

$\text{Al/V} = 50/1$; $\text{Al/less monomer} = 5 \times 10^{-2}/1$ (g-atom/mole).

IP : Isoprene. PD : Pentadiene-1,3. BD : Butadiene-1,3. AN : Acrylonitrile.

* $r_{\text{IP}}=0.29$; $r_{\text{AN}}=0.05$ at 50°C ; $r_{\text{BD}}=0.53$; $r_{\text{MMA}}=0.06$ at 5°C .

halide together with vanadium compound.³⁸⁾ The experimental results of the copolymerization of the diene with the polar vinyl monomer are shown in Table II. Here, the mixing order of reagent was very important for controlling the catalyst activity. When the order as the monomer-AlEtCl₂-VOCl₃ is adopted, the copolymers obtained were always 1:1 in the composition, irrespective of the initial monomer feed ratios as shown in Table II.

2. Alternating Copolymerization of Butadiene with Acrylonitrile

The most interesting results are obtained in the copolymerization of butadiene with acrylonitrile under a mild condition with the aid of alkylaluminum halide-vanadium or titanium compound system. In this way an alternating copolymer of high molecular weight are prepared in high yield, and only a soluble copolymer is available by selecting the transition metal compounds such as VOCl₃ and VO(acac)₂. Otherwise insoluble powdery polymer results in. The catalytic activity for the alternating copolymerization of butadiene with acrylonitrile is clarified as shown in Table III.

The mixing order of reagent was influential on the catalyst activity, *e.g.*, the AlEtCl₂-monomer-V or Ti compound, or the V or Ti compound-monomer-AlEtCl₂ is the suitable one. A simple mixing of EtAlCl₂ and V compounds in the absence of monomer does not afford an alternating polymer. The vanadium compounds such as V(acac)₃, VO(acac)₂ and VOCl₃ are most effective.

The catalytic activity of aluminum compounds is also summarized in Table IV.

Table III. Effects of Vanadium and Titanium Compounds on the Copolymerization of Butadiene with Acrylonitrile in Toluene at 0°C

BD/AN (mole/mole)	V or Ti compound	Catalytic activity ($\times 10^{-2}$)	$[\eta]$ (dl/g)	Gel (%)
2	none	2	—	Ca. 90
2	VO(Ot-Bu) ₃	95	0.83	8
2	VO(OEt) ₃	60	—	—
2	VO(acac) ₂	68	1.56	Ca. 0
2	V(acac) ₃	63	1.58	5
2	VO(Ot-Bu) ₂ Cl	102	1.09	30
2	VO(Ot-Bu)Cl ₂	77	1.31	5
2	VOCl ₃	60	1.40	Ca. 0
2	VCl ₄	43	—	—
1	VO(OAc) ₂	22	—	—
1	VO-naph.	43	—	—
2	VCl ₃	38	—	—
2	V ₂ O ₃	28	—	—
2	Ti(O-nBu) ₄	32	1.48	65
2	TiO(acac) ₂	28	—	—
2	TiCl ₄	22	1.62	38
1	Ti oxalate	28	—	—
1	TiH ₂	28	—	—

Al/V or Ti=50/1; Al/Total monomer=1.7–2.0 $\times 10^{-2}$ /1 (g-atom/mole).

Alternating Copolymerization of Butadiene-1,3 with Acrylonitrile

Butadiene and acrylonitrile are copolymerized by alkylaluminum halide alone, or more effectively by alkylaluminum halide with vanadium compound. The efficiency of the binary catalytic system as shown in Table IV decreases in the following order.

Table IV. Effects of Aluminum Compounds on the Copolymerization of Butadiene with Acrylonitrile in Toluene at 0°C

Aluminum compound	Catalytic activity ($\times 10^{-2}$)	$[\eta]$ (dl/g)
none	0	—
AlEt ₃ ·AN* ¹	0* ⁴	—
AlEt ₂ Cl·AN* ¹	12* ²	—
Al ₂ Et ₃ Cl ₃ ·AN	67	2.06
Al ₂ Et ₃ Br ₃ ·AN	88	1.64
Al ₂ (iBu) ₃ Br ₃ ·AN	17	—
AlEtCl ₂ ·AN	95	1.43
AlCl ₃ ·Et ₂ O	trace* ³	—

Al/VO(t-BuO)₃=50/1; Al/total monomer= 1.7×10^{-2} /1 (g-atom/mole).

*¹ Solvent : (ClCH₂)₂. Al/V = 20/1

*² Grease.

*³ Rubbery solid estimated to be 1:1 copolymer from its IR spectrum.

*⁴ Polymer could obtain after 2 – 3 days.

Table V. Influence of Mixing Order of Reagents at -78°C in the Case of the AlEtCl₂-VOCl₃ System*¹

Mixing order* ²	Catalytic activity ($\times 10^{-3}$)
Tol. -AN-BD-Al-V	83
Tol. -AN-Al-BD-V	77
Tol. -AN-Al-V-BD	83
Tol. -AN-V-Al-BD	72
Tol. -BD-Al-AN-V	72
Tol. -BD-Al-V-AN	very low* ³
Tol. -BD-V-AN-Al	83
Tol. -BD-V-Al-AN	very low* ³
Tol. -Al-AN-BD-V	66
Tol. -Al-AN-V-BD	66
Tol. -Al-BD-AN-V	66
Tol. -Al-V-AN-BD	trace
Tol. -Al-V-BD-AN	trace
Tol. -V-AN-Al-BD	88
Tol. -V-AN-BD-Al	72
Tol. -V-BD-AN-Al	83
Tol. -V-BD-Al-AN	very low* ³

*¹ BD/AN (in feed) = 1.7/1 (mole/mole) ; solvent=toluene; solvent/total monomer=2/3 (vol/vol); Al/total monomer= 1.8×10^{-2} /1 (g-atom/mole); Al/V=50/1 (g-atom/g-atom) ; catalysts were prepared at -78°C.

*² Tol.=toluene ; Al=AlEtCl₂ ; V=VOCl₃.

*³ Liquid polymer.



The order may be associated with the acidity of the aluminum compound. The catalytic activity is also markedly influenced by the mixing order of the monomers and catalyst components. Of course, the alkylaluminum halide could be utilized in the preformation of a complex with acrylonitrile. As a general rule, the effective catalyst is prepared only when the catalyst components are mixed in the presence of acrylonitrile as shown in Table V. From these data it would be deduced that the aluminum compound was complexed with acrylonitrile and an active species for the copolymerization was cultivated by adding the vanadium compound into aluminum compound-acrylonitrile complex. The maximum activity of $\text{AlEtCl}_2 \cdot \text{AN} - \text{VO}(\text{t-BuO})_3$ system was observed at a ratio of about 1:1/10 under these conditions.

3. Alternating Copolymerization of Butadiene with Acrylonitrile initiated by Organic Peroxide

The conventional radical copolymerization of diene with acrylonitrile in the presence of a metal halide was already investigated.^{35,40)} The copolymer was merely 1:1 in the composition and was sparingly soluble in acetone *etc.* However, the microstructure of the copolymer was not clearly indicated. Besides, the copolymer is mostly insoluble even in dimethylformamide. This is probably ascribed to a cross linked structure.

In order to elucidate the microstructure of the diene-acrylonitrile copolymer and to prevent the gel formation, the copolymerization of butadiene with acrylonitrile in the presence of such Lewis acid as AlCl_3 , SnCl_4 or ZnCl_2 with a vanadium compound and an organic peroxide has been studied.³⁹⁾ The copolymer obtained was fairly soluble in chloroform. The alternating tendency was rather increased by adding the vanadium compound. The part of result of copolymerization is listed in Table VI. These data and other results⁴³⁾ suggest that the vanadium compound may have three important effects on the polymerization. That is, the vanadium compound seems to play an important role on initiation, propagation and transfer reaction.

Precedingly, the alternating copolymerization of butadiene with acrylonitrile in the presence of organometallic compounds such as $\text{AlEt}_m\text{Cl}_{3-m}$ -vanadium compounds³⁸⁾ or AlCl_3 -vanadium compound-organic peroxide³⁹⁾ was mentioned. A similar

Table VI. Copolymerization of Butadiene with Acrylonitrile by Lewis acid-BPO- VOCl_3 System in CH_2Cl_2 at 25°C

Lewis acid (mmole)	BPO (mmole)	VOCl_3 (mmole)	Yield (%)	$[\eta]$	AN content in polymer (%)
AlCl_3 1	0.5	—	14.4	—	49
AlCl_3 1	0.5	1.0	6.6	0.70	49
SnCl_4 1	0.5	—	32.8	—	45
SnCl_4 1	0.5	1.0	17.8	0.54	50
ZnCl_2 1	0.5	—	17.4	0.92	40
ZnCl_2 1	0.5	1.0	10.0	0.54	50

alternating copolymer is also obtained in the presence of $\text{AlEt}_3\text{-CrOCl}_2$ ³⁹⁾ or in the presence of a Lewis acid together with UV irradiation.⁴¹⁾ An alternating copolymerization mechanism will be discussed in detail in near future.

4. Kinetics

The kinetic studies of the alternating copolymerization of SO_2 or maleic anhydride with olefinic compound have been reported.^{19~24)} The propagation probably proceeds via a cross attacking mechanism⁴²⁾ or by an attacking of chain end to a monomer pair.²³⁾ Same mechanism seems to exist when butadiene and acrylonitrile copolymerize in the presence of an organometallic compounds and vanadium compounds. In this case, we expect that the active center for polymerization is not an usual ionic species but rather is a radical one.²⁹⁾ However, the polymerization was not inhibited by the radical scavenger such as sulfur and was only slightly retarded by benzoquinone, phenyl- β -naphthylamine and DPPH.²⁹⁾

The alternating copolymerization of butadiene with acrylonitrile is carried out in the excess of acrylonitrile monomer without solvent to study in homogeneous solution system using the $\text{AlEtCl}_2\cdot\text{AN}\cdot\text{VOCl}_3$ catalyst system. The studies in a solvent such as toluene are rather complicated with lowering of alternating tendency.²⁹⁾ Imoto *et al.* already mentioned that the equilibrium constant of the complex formation of acrylonitrile and a metal halide was markedly influenced by the solvent used.⁶⁾ Such a feature of the mechanism is now considered in the kinetic studies of the alternating copolymerization of butadiene with acrylonitrile.⁴³⁾

The copolymerization rate at 0°C was well fitted in with a first order reaction. The initial rate at 0°C (R_{p0}) is approximated by equation (2).

$$R_{p0} \propto [\text{BD}][\text{Al}]^{3/2}[\text{V}]^{1/2} \quad (2)$$

The apparent activation energy ΔE and the pre-exponential factor, A at the polymerization temperature from 0°C to 30°C were evaluated to be 13 Kcal/mole and 1×10^8 l/mole \cdot hr, respectively.

The molecular weight of the alternating copolymer formed is increased with conversion. The molecular weight distribution and its changes during polymerization offer good promise of providing new experimental information that has not been readily obtained with other system. Szwarc *et al.* pointed out that a normal distribution of molecular weights will ultimately result from polymerization of a living polymer.⁴⁴⁾ However, if the depropagation reaction is slow and initiation is rapid, poisson distribution will be formed at initial stage of polymerization.^{44,45)}

The experimental result measured by GPC method showed²⁹⁾ that the MW distribution in the butadiene-acrylonitrile copolymer prepared using the $\text{AlEtCl}_2\cdot\text{AN}\cdot\text{VOCl}_3$ catalyst looks like that of an asymmetrical type at the copolymer yield of about 50% and the M_w/M_n ratio is lower than that of the copolymer obtained by the conventional emulsion polymerization method. The studies of the variation of the molecular weight distribution at various degree of conversion in the presence of a suitable chain transfer agent may be make clear the reaction mechanism in detail. The molecular weight of the polymer, however, decreased with increasing catalyst concentration. That is, the variance of the molecular weight of the copolymer resembles that of successive type polymerization.

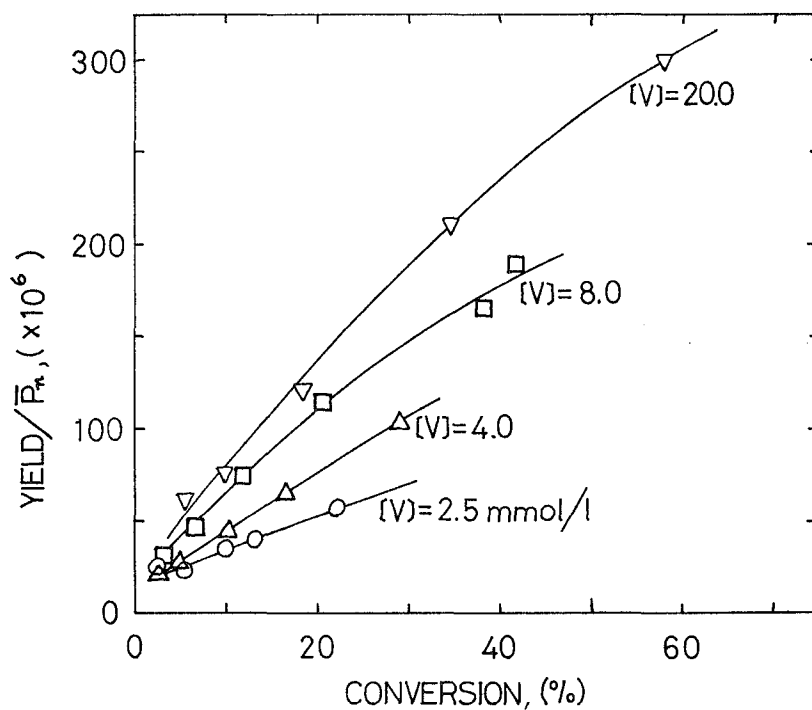


Fig. 1. Estimated number of polymer chain as a function of conversion with variation of vanadium concentration at constant aluminum concentration. $[\text{Al}]=80.0 \text{ mmol/l}$.

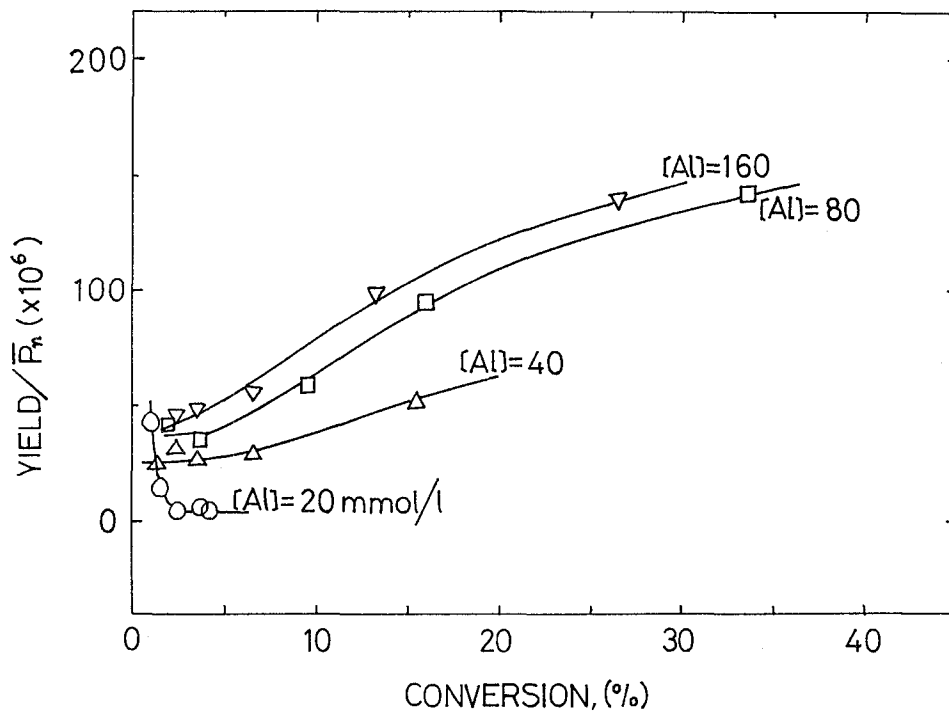


Fig. 2. Estimated number of polymer chain as a function of conversion with variation of aluminum concentration at constant vanadium concentration. $[\text{V}]=8.0 \text{ mmol/l}$.

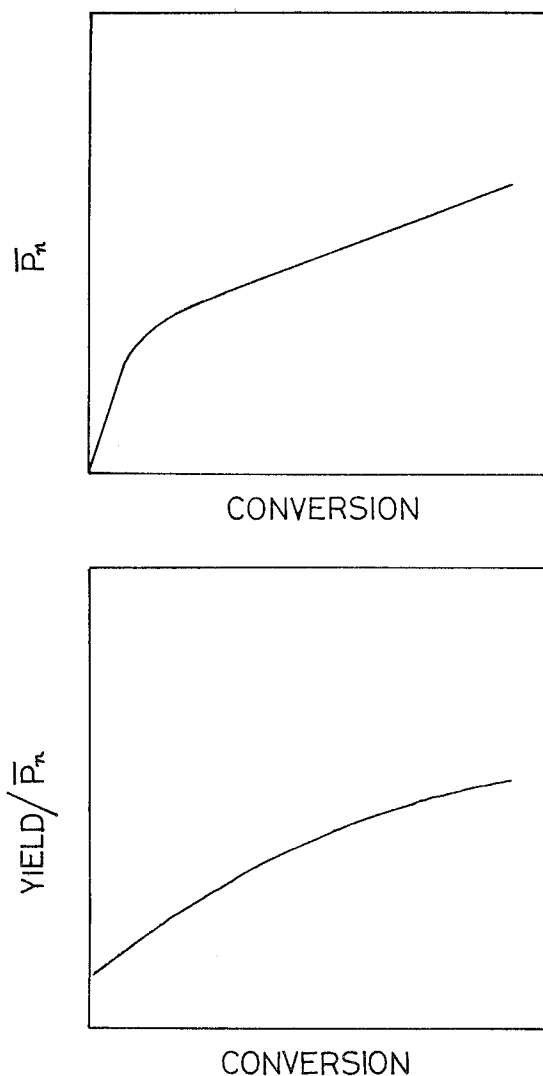


Fig. 3. Schematic diagram of the characteristics of alternating copolymerization.

The number of the copolymer chain are usually changed during polymerization as shown in Figure 1. This may arise from chain transfer to the catalyst, since the vanadium and aluminum compound enhance the transfer.

The number of the copolymer chain estimated in terms of $[M_p]/\bar{P}_n$ seems to increase in the course of polymerization as shown in Figure 2.

The most effective species for the copolymerization seems to be produced at Al/V ratio of about 10. And the nature of the active species may also depend on the polymerization conditions such as the concentration of the Al compound and polymerization temperature.²⁹⁾

According to Kagiya *et al.*,⁴⁶⁾ our experimental results are schematically expressed as shown in Figure 3. As shown above, this copolymerization would be classified as

a so-called rapid-initiation, non-stationary, successive type polymerization. These figures also indicate that the \bar{P}_n and $[M_p]/\bar{P}_n$ in the alternating copolymerization of butadiene with acrylonitrile is mainly under the rule of a transfer reaction to the monomer and catalyst. The vanadium compounds seems to take parts in the regeneration of the catalyst.

Detailed investigations are now in progress

IV. PROPERTIES OF THE ALTERNATING COPOLYMER OF BUTADIENE WITH ACRYLONITRILE

1. Infrared Spectrum of the Alternating Copolymer^{38,47)}

The infrared spectrum of the alternating copolymer of butadiene with acrylonitrile indicates that the butadiene unit is linked to each other with a high trans-1,4 configuration as shown in Figure 4. The copolymer was prepared by the $AlEtCl_2 \cdot An-VOCl_3$ system at 0°C. Some characteristic absorptions are observed at 2240 cm^{-1} assignable to the nitrile group and at 970 cm^{-1} assignable to the trans-1,4 linkage of the butadiene unit, but the absorption assignable to the vinyl or cis-1,4 linkage of the butadiene unit is either scarcely recognizable or entirely unobservable. The microstructure of butadiene units was also evaluated by Morero's method⁴⁸⁾ to be the trans-1,4 of 98%, vinyl of 2% and cis-1,4 of nearly 0%. The high selectivity for the diene linkage suggests a coordination mechanism of the diene monomer.

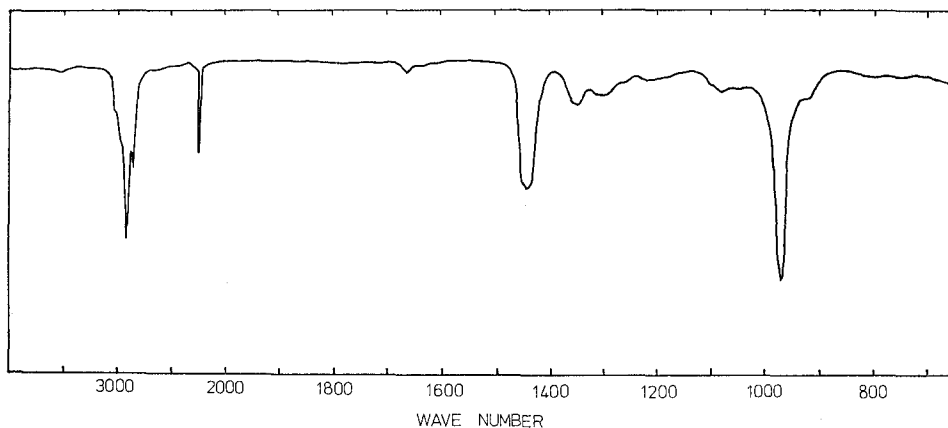


Fig. 4. Infrared spectrum of the alternating butadiene-acrylonitrile copolymer prepared by the $AlEtCl_2 \cdot AN-VOCl_3$, (Film).

2. High Resolution NMR Spectrum of the Alternating Copolymer^{38,47)}

The high resolution NMR spectrum of the alternating copolymer of butadiene with acrylonitrile in comparison with the conventional radical copolymer is illustrated in Figure 5.

The characteristic bands of the copolymers are briefly expressed in Figure 6. The spectrum of the alternating copolymer (c) lacks the absorption at 7.87τ (3), but

Alternating Copolymerization of Butadiene-1,3 with Acrylonitrile

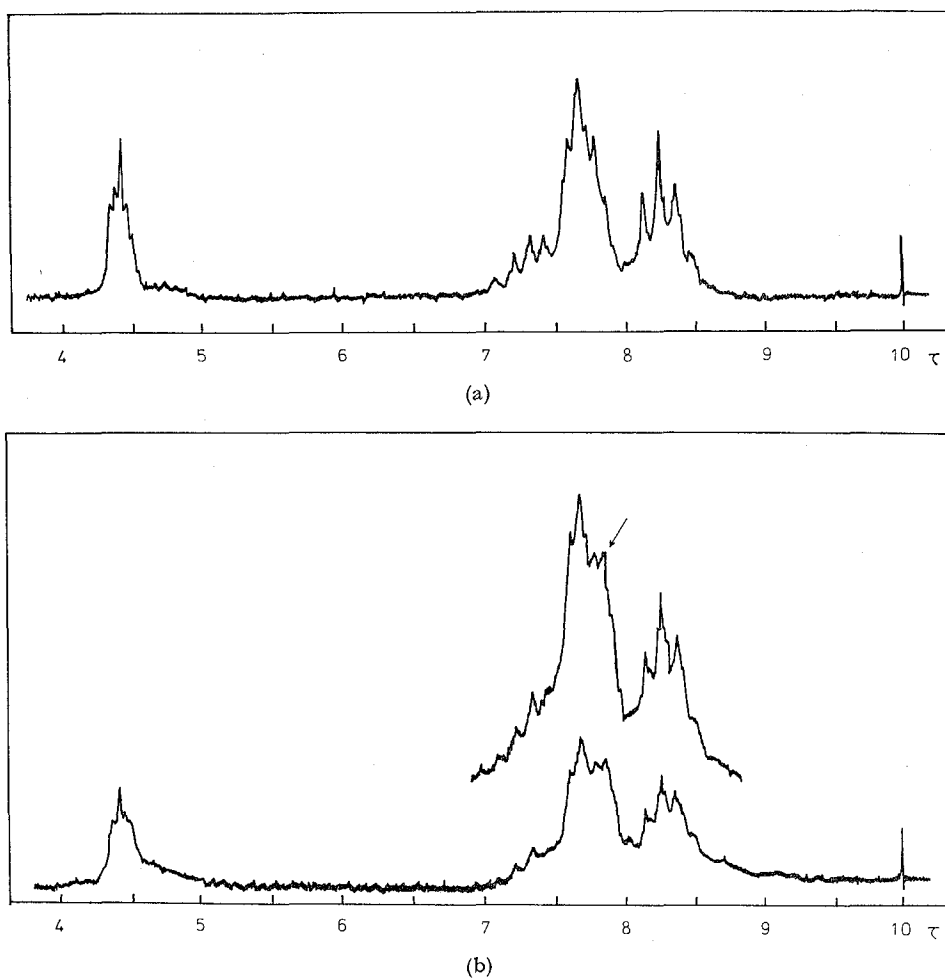


Fig. 5. NMR spectra of butadiene-acrylonitrile copolymer prepared by the $\text{AlEtCl}_2 \cdot \text{AN} \cdot \text{VOCl}_3$ (a) in comparison with the conventional radical process (b).

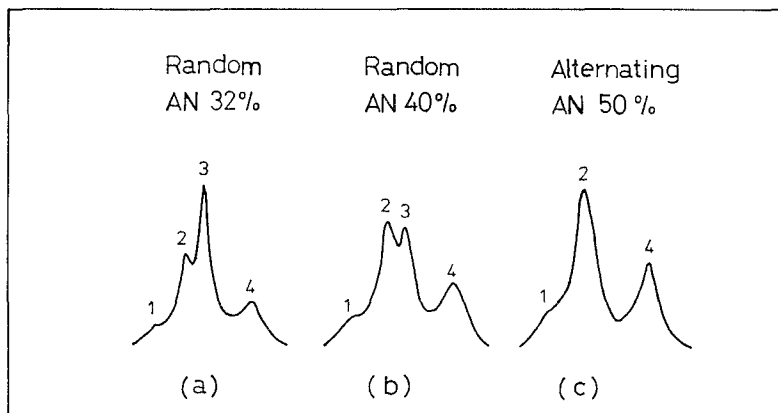


Fig. 6. Schematic-diagram of NMR spectra of butadiene-acrylonitrile copolymer. The spectra at figures are assigned as noted in Table VII.

this absorption band is clearly observed in the spectra of the random copolymers (a), (b) and increases with increasing content of butadiene-to-butadiene bond in the copolymer as seen in Fig. 6-(a).

The assignments of the chemical shifts are tentatively given in Table VII. The peak assignable to methylene protons of the butadiene unit in a butadiene-acrylonitrile diad of the alternating copolymer is expected at 7.72τ . The peak at 7.87τ assignable to those in a butadiene-butadiene diad is not found even by 100 Mc NMR.

These results suggest the high regularity in alternation of monomeric units distribution in the copolymer.

3. X-Ray Diffraction Analysis of the Alternating Copolymer^{38,47)}

The infrared spectra and NMR spectra of the alternating copolymers indicated that the alternating copolymer has a high regularity in the structure of the chain. The regularity is also estimated from the x-ray diffraction analysis of the alternating copolymer. The copolymer chains are oriented and crystallized in highly elongated state as shown in Figure 7.

The d spacing is estimated to be 7.27 \AA , which seems to correspond to the butadiene-acrylonitrile repeating unit.

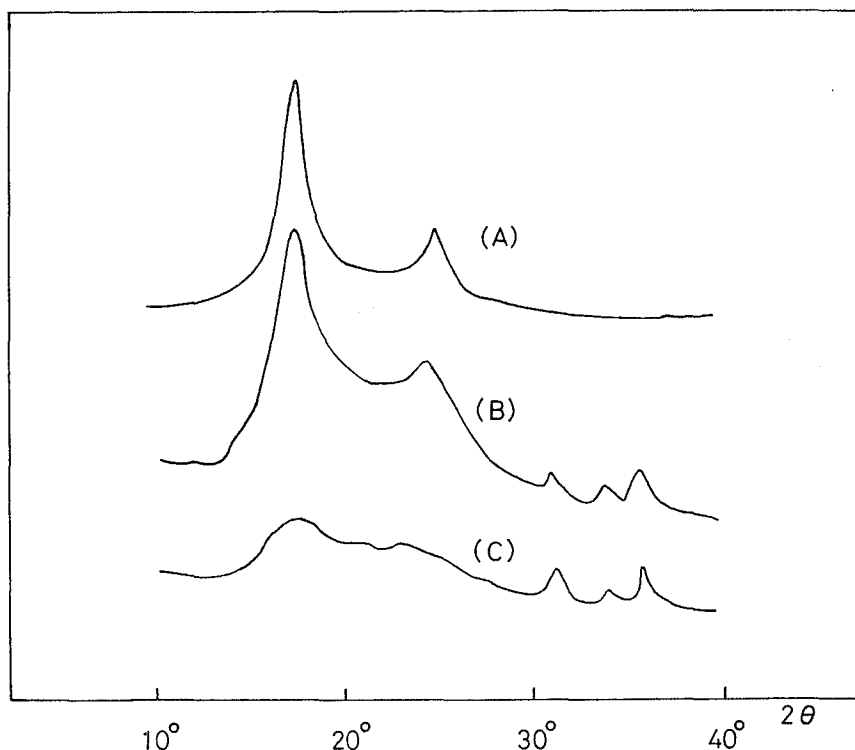


Fig. 7. Scattered x-ray intensity along equator line.

- (A) Raw polymer of the alternate at 400% elongation.
- (B) Cured rubber of the alternate at 220% elongation.
- (C) Cured rubber of the random at 190% elongation.

Alternating Copolymerization of Butadiene-1,3 with Acrylonitrile

Table VII. Assignment of NMR Spectra

Group		Random	Alternate	PBD	PAN
		AN : 39%	AN : 50%		
-CH=CH-	B-A	4.45 τ	4.45 τ	— τ	— τ
	B-B	4.59	—	4.69	—
-CH-		7.42 ⁽¹⁾	7.35 ⁽¹⁾	—	7.0
CN					
=CH-CH ₂ -	B-A	7.72 ⁽²⁾	7.70 ⁽²⁾	—	—
	B-B	7.87 ⁽³⁾	—	8.02	—
-CH ₂ -CH-		8.30 ⁽⁴⁾	8.27 ⁽⁴⁾	—	8.1
CN					

Table VIII. Compounding Formula for BD-AN Copolymer

Materials	Parts by weight
Polymer	100
Carbon black SRF	45
Zinc oxide	5
Stearic acid	1
Antioxidant PBNA	1
Accelerator NOBS sp.	1
Sulfur	1.5

Table IX. Properties of the Cured Rubber

	Alternate		Random (AN : 48%)	
	60'	90'	60'	90'
Cure time (145°C)				
Original state				
H _S (JIS)	73	74	86	85
M ₁₀₀ (kg/cm ²)	43	43	105	114
T _S (kg/cm ²)	237	243	194	205
E _B (%)	400	400	210	200
Hot state (110°C)				
T _S (kg/cm ²)	58		50	
E _B (%)	340		210	
Oil resistance (Oil : JIS''B'',* R.T.×48hr)				
Swell (%)	112	112	112	112
T _S (kg/cm ²)	147	153	97	112
E _B (%)	300	290	150	160

* Isooctane/toluene = 70/30.

4. Mechanical Properties of the Alternating Copolymer of Butadiene with Acrylonitrile

The vulcanization of the alternating copolymer using sulfur has been reported.⁴⁷⁾ The example of the compounding recipe is shown in Table VIII.

Representative properties of some vulcanizates of the alternating copolymer ($[\eta] = 1.8$ dl/g, 30° C in DMF) are listed in Table IX in comparison with the conventional nitrile rubber prepared by emulsion polymerization.

The results of the tensile test indicate that the alternating copolymer is rather lower in hardness and modulus than those of random one. However, the tensile strength and ultimate elongation were found to be considerably greater. These features mean that the alternating copolymer is much more stronger than the random one in spite of its soft flexible molecular chain. The crystallization at high extension enhances the tensile properties. The characteristics can be recognized more explicitly from the stress-strain curves as shown in Figure 8.

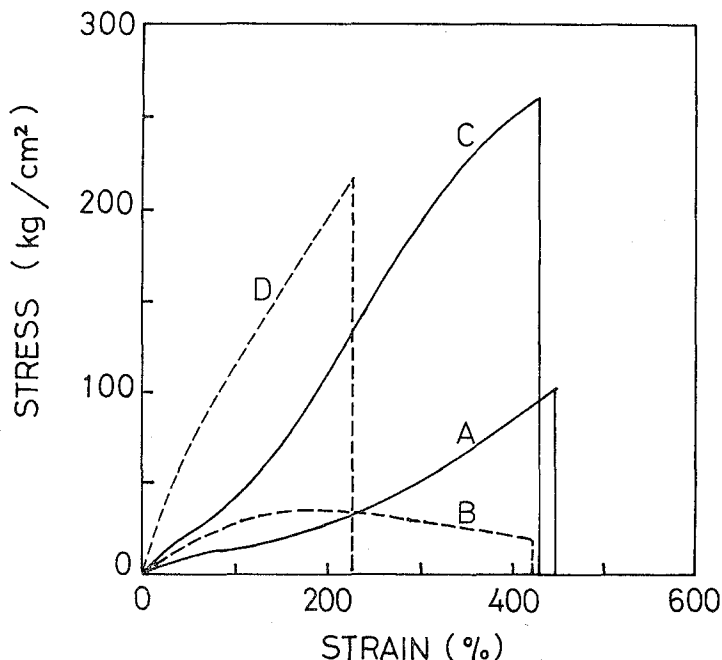


Fig. 8. Stress-strain property.

- (A) Raw polymer of the alternating BD-AN copolymer of a η_{sp}/c of 6.5 at 30°C in 0.5% solution of dimethyl formamide.
- (B) Raw polymer of the random reference.
- (C) Cured rubber of the alternating sample.
- (D) Cured rubber of the random reference.

The alternating one was superior to the random one in rebound elasticity at elevated temperature. The alternating copolymer was lower in the in-phase modulus (E') and the loss modulus (E'') and exhibited lower loss tangent at higher temperature. The oil resistance of the alternating copolymer was not found to differ so far from the conventional one from the swelling experiment.

However, the alternating copolymer was superior to the random one in tensile properties after swelling.

Much interesting work, both fundamentally and practically useful, remains to be done. However, it can be pointed out that the general properties of the alternating copolymer, such as the oil resistance, the elasticity and the toughness, are superior to those of the random copolymer. These favorable features of the alternating copolymer are due to high regularity of alternation in its chain structure.

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